EFFECTS OF START-UP SOLVENT ON COMPOSITION OF RECYCLE LIQUEFACTION PRODUCT SLURRY FROM LOW-RANK COALS

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Introduction

As part of the on-going research in the liquefaction of low-rank coal, the University of North Dakota Energy Research Center (UNDERC) carried out two bottoms recycle runs. The purpose of these 40 pass runs was to investigate the effect of two different start-up solvents on the composition of the product from pass to pass, especially the bottoms portion used as recycle solvent, and the final lined-out composition of the product.

Runs 101 and 103 were carried out in the bottoms recycle mode in the Continuous Processing Unit (CPU) (1). Zap, North Dakota lignite from the Indian Head mine was introduced at 5 lbs/hr as a 30% slurry (wt % as-received coal) in recycle feed with H_2S addition in both runs. The nominal temperature was 440°C and the nominal pressure was 4000 psig H_2/CO (95/5). The startup solvent for Run 101 was a typical anthracene oil, A04, purchased from Crowley Tar Products, NY, previously described (2,3). Run 103 was started up with a Process Development Unit (PDU) recycle solvent obtained from the University of North Dakota Chemical Engineering Department's Project Lignite (4). The PDU solvent was derived from Zap, North Dakota Indian Head lignite. It has been characterized in detail (3). A short summary of the relevant properties of the two startup solvents appears in Table I. Both solvents provided adequate operability of the CPU and were greater than 95% distillable. These two startup solvents were chosen because they differ in several important ways. The PDU solvent contained about seven times more total alkanes and ten times more n-alkanes than the A04 solvent (Table I). The PDU solvent also contained a higher concentration of methylated and other alkylated aromatic hydrocarbons than A04. For example, 2- and 3-methylphenanthrene are present in the PDU solvent at 4.6 and 3.0 times their concentrations in A04. The PDU solvent also contains hydroaromatics (such as dihydro-, tetrahydro- and octahydro-phenanthrene, dihydropyrene, and tetrahydrofluoranthene) and phenols (6.2%). A04, deficient in both hydroaromatics and phenols, is composed mainly of unsubstituted aromatic hydrocarbons including larger amounts of aromatic compounds with more than three fused rings (i.e., chrysene and benz(a)anthracene) than the PDU solvent. These differences in composition are expected to affect the solvating power of the solvent toward coal and coal-derived products. The difference in reactive nature of the solvents at high temperature and pressure is expected to lead to different initial products.

The liquefaction products were examined from pass to pass in order to follow the compositional changes as the reaction proceeded toward steady-state composition (lineout) and to determine whether the products were chemically the same for both runs after 40 reactor passes.

Table I. Properties of Startup Solvents A04 and UND PDU Solvent Used In CPU Runs 101 and 103

	A04	PDU
Elemental Analysis:		
% C	90.33	82.36
H	6.54	7.89
N	0.83	0.21
S	0.57	1.19
O (by difference)	1.73	2.49
Ash, %	0.03	1.43
Water, %	0.20	4.43
Selected Organic Component Analysis, wt %:		
n-alkanes	0.6	6.8
total alkanes	2.2	13.9
Selected Hydrocarbons and Ethers:		
naphthalene	0.75	0
2-methylnaphthalene	1.44	0.14
acenaphthene	9.54	0.08
phenanthrene	16.6	6.99
dibenzofuran	6.67	0.39
3-methylphenanthrene	0.66	3.06
2-methylphenanthrene	0.84	2.55
fluoranthene	0.52	0.82
pyrene	6.87	0.46
fluorene	6.67	0.36
benzo(a)anthracene	0.26	0.06
chrysene	0.27	0.16
9,10-dihydrophenanthrene	0	0.23
octahydrophenanthrene	0	0.02
1,2,3,4-tetrahydrophenathrene	0	0.18
4,5-dihydropyrene	0	0.44
1,2,3,4-tetrahydrofluoranthene	0.01	0.06
polars (phenols, base and polar aromatics)	18.4	21.4
phenols	0	6.2

Our previous efforts were concentrated on analysis of distillable portions of the products from earlier runs which averaged approximately 13 passes (5). When we investigated these runs we noticed that some irreversible changes caused by heating had occurred to the vacuum bottoms during the ASTM D-1160 distillation. We carried out several preliminary separations using Soxhlet extraction, sonication and sonication with heat, none of which proved satisfactory for this study. A method was then selected for separation of the slurry that excluded all severe handling of the product to avoid changes in the heavy product composition during separation.

The preliminary characterization of the separated heavy products and their composition as compared with the composition of the oils are the focus of this report. Changes in the startup solvent as it reacts with coal and is diluted by coal-derived products are discussed with emphasis on the heavy components. Differences between the two runs started up with different solvents are described.

Experimental

The method chosen to separate the product slurry is based on solubilities at room temperature (Figure 1). This separation yielded a pentane soluble, volatile oil fraction (oil), a pentane insoluble, methylene chloride soluble heavy fraction (soluble heavy ends), and a methylene chloride insoluble fraction (insoluble heavy ends), Table II. Further fractionation of the oils and soluble heavy ends from pass 40 was carried out by silica gel open column chromatography. Three fractions were collected: alkanes (eluted with pentane, isooctane, pentane), aromatics (eluted with methylene chloride), and polars (eluted with methanol) (Table III). The chromatographic method involved 100 g Aldrich Grade 12 28-200 mesh silica gel activated at 250°C for 24 hours packed dry between two glass wool plugs in a Pyrex column that had a 75-100 μ fritted glass plate. The silica gel was wetted with HPLC grade pentane and then loaded with ~1 gram of sample. Elution was in the following sequence with HPLC grade solvents: 150 ml pentane, 100 ml isooctane, 50 ml pentane, 250 ml methylene chloride, and 100 ml methanol. The first three listed elute alkanes, the fourth elutes aromatics and the polar compounds are eluted with the fifth.

Characterization studies were carried out on the fractions using elemental analysis, tetrahydrofuran (THF) solubility, thermogravimetric analysis (TGA), size exclusion high performance liquid chromatography (mobile phase THF, UV and refractive index detection), IR spectrometry, 200 MHz ^{1}H NMR and 50 MHz ^{13}C NMR spectrometry, capillary GC/MS and direct probe MS.

Results and Discussion

The variation in composition of the product slurries from Runs 101 and 103 during 40 recycle passes is shown in Figure 2 and Table II.

Insoluble Heavy Ends. The insoluble heavy ends increased during both runs. A steadier, earlier increase was seen during Run 101 (Figure 2), coinciding with the increasing viscosity. During Run 101 the reactor was "blown down" only once (pass 25) to remove accumulated reactor solids resulting in a rapid drop in viscosity. The viscosity then rose slowly until pass 40 where a rapid increase was seen (3). The insoluble heavy ends increased more slowly during Run 103. This slower increase may be related to the much lower viscosity observed

Table II. Composition of Recycle Slurries (Wt %) During CPU Runs 101 and 103

Fractions	Pass No. 0	7	19	30 (31)	40
Oil:					
101	94.5	70.9	50.2	54.7	48.4
103	88.3	67.0	59.0	46.3	46.1
Soluble Heavy Ends:					
101	4.1	14.3	19.9	16.4	16.1
103	2.7	18.9	19.6	16.2	19.7
Insoluble Heavy Ends:*					
101	0.04	8.6	19.1	27.6	29.8
103	3.1	9.9	12.7	24.4	25.6
Total % Recovery:					
101	98.6	93.8	89.2	98.7	94.3
103	94.1	95.8	91.3	86.9	91.4
Ash:					
101	0.03	6.6	10.8	11.2	11.4
103	4.4	6.9	9.8	13.0	11.5

*Includes mineral matter.

Table III. Silica Gel Column Fractionation of CPU Runs 101 and 103 Pass 40 Oils and Soluble Heavy Ends (Wt %)

	101 Pass 40		103 Pass 40	
	Soluble Heavy Ends	Oil	Soluble Heavy Ends	Oil
Alkanes	0.1	5.6	0.6	8.0
Aromatics	56.2	59.1	45.0	58.6
Polars	35.3	28.1	36.6	31.2
% Recovery	92.6	92.8	82.2	97.8

during Run 103. The viscosity was controlled during Run 103 by scheduling reactor blowdown every twelfth pass. Direct insertion probe MS heating profiles of the insoluble heavy ends from Runs 101 and 103 gave non-quantitative profiles of the small percentage of the material that could be analyzed by this method. The insoluble heavy ends sample from Run 101 gave a prominent peak that volatilized early in the run. This peak gave a mass spectrum that appeared to be identical with that of 1,2'-binaphthyl. This component was not present in the insoluble heavy ends from Run 103. It was not a prominent component of the soluble heavy ends from either run. After subtracting the ash content and the THF soluble portion of the heavy ends, 7.5% of Run 101 and 6.7% of Run 103 is intractable THF insoluble organic matter (Table IV).

Soluble Heavy Ends. The soluble heavy ends also increased gradually from pass to pass during both Runs 101 and 103 as the coal-derived materials began to replace the >91% soluble startup solvents (Figure 2 and Table II) until pass 40 where the sum of the insoluble and soluble heavy ends reached about 45% to 46%. This leaves 48.4% (Run 101) and 46.1% (Run 103) oils as products at pass 40 (Figure 2 and Table II).

Characterization of the soluble heavy ends is much more difficult than the characterization of distillable oils which can be easily separated by capillary GC and identified by GC, GC/MS and NMR comparisons with known standard compounds. However the soluble heavy ends resemble the oils in some very important ways. They can be separated by simple column chromatography on silica gel into fractions easily identified as alkanes (δ0.5-1.4), aromatics (δ7.2-8.7), and polars (δ6.2-7.2) by 200 MHz ^{1}H NMR (Figure 3) and 50 MHz ^{13}C NMR spectrometry. The soluble heavy ends from Runs 101 and 103 partitioned differently with our separation (Table III). Run 103 produced more C-9 and larger alkanes in the heavy and oil fractions than Run 101. Small contamination of both alkane fractions by phthalates occurred (note extraneous peaks on Figure 3, top right). Small amounts of phthalate contaminants were accidentally introduced into the slurry. They appear in all three column fractions, but mainly in the heavy ends polar fraction of Run 101. Run 103 also produced more polars in the oil and heavy fractions than Run 101 (Table III). Run 101 produced slightly more aromatic hydrocarbons than Run 103.

Soluble Heavy Ends-Aromatic Fractions. Differences between aromatic fractions of the soluble heavy ends of Runs 101 and 103 may be seen by inspection of the elemental analyses (Table V), the ^{1}H NMR spectra (Figure 3, middle), the IR spectra (not shown), TGA volatiles, and the average molecular weight maxima (Table IV). Direct insertion probe MS heating profiles from 30° to 350°C at 5°/min obtained at 10 ev and 70 ev were compared for samples of aromatic fractions of the soluble heavy ends Run 101 and 103. During the first part of the heating profiles small amounts of materials with masses recognizable as common hydrocarbons were noted. These included such masses as 128,142 (probable naphthalenes), 178,192 (phenanthrenes) and 202,216 (pyrenes) which were seen in the heavy aromatic fractions of both Runs 101 and 103. Masses 168,182 and 196 (probable dibenzofurans) were much more prominent in the heavy aromatics from Run 103 than Run 101. These parent ions, present in both high- and low-voltage mass spectra, are probably small hydrocarbons and ethers partitioned into the heavy fraction during our initial solubility separation. As the heating progressed a large number of masses giving the maximum ion current

Table IV. Properties of Oils, Soluble Heavy Ends, and Insoluble Heavy End Fractions of CPU Runs 101 and 103, Pass 40

Sample	THF Insoluble (wt %)	Nonvolatiles (TGA) (wt %) (T_{max})	Average MW Maxima (Size Exlusions HPLC)
Total Samples:			
101 Sol. Heavy Ends	0.00	32.52 (800C)	10,000, 1200, 475
103 Sol. Heavy Ends	0.00	31.62 (800C)	10,000, 1200, 475, 280, 240
101 Oil	0.00		1200, 540, 420, 360
103 Oil	0.00		620, 505, 360, 210, 340, 290, 260
Silica Gel Column Fractions 3 (aromatics):			
101 Sol. Heavy Ends	0.00	42.69 (500C)	1200, 1000, 550
103 Sol. Heavy Ends	0.00	36.25 (500C)	10,000, 1200, 600, 450, 320
101 Oil	0.00	2.83 (500C)	610, 385, 345, 320, 220, 160
103 Oil	0.00	1.75 (500C)	330, 310, 220, 210, 170, 150
Silica Gel Column Fractions 4 (polars):			
101 Sol. Heavy Ends	1.97	31.98 (500C)	13,000, 1350, 520, 450
103 Sol. Heavy Ends	4.61	17.75 (500C)	1200, 480, 430, 380
101 Oil	0.00	11.31 (500C)	15,000, 1100, 680, 540, 450, 360, 330, 150
103 Oil	4.46	13.53 (500C)	16,000, 1000, 520, 380, 360, 250, 200
Insoluble Heavy Ends:			
101	63.5 (18.9% of slurry)		
103	71.0 (18.2% of slurry)		

Table V. Elemental Analyses of Products from CPU Runs 101 and 103, Pass 40

Sample	Column Fraction	Elemental Analysis C	H	N	O	C-100 Formula
101 Oils	Aromatics	85.06	7.34	0.28	7.32	$C_{100}H_{102.82}N_{0.28}O_{6.46}$
101 Sol. Heavy Ends	Aromatics	88.89	5.77	1.43	3.91	$C_{100}H_{77.30}N_{1.38}O_{3.30}$
103 Oils	Aromatics	88.56	7.66	1.67	2.11	$C_{100}H_{103.11}N_{1.61}O_{1.79}$
103 Sol. Heavy Ends	Aromatics	90.44	5.81	1.21	2.54	$C_{100}H_{103.11}N_{1.61}O_{1.79}$
101 Oils	Polar	77.96	7.66	1.33	13.05	$C_{100}H_{117.09}N_{1.46}O_{12.57}$
101 Sol. Heavy Ends	Polar	70.63	4.94	2.36	22.07*	$C_{100}H_{83.33}N_{2.86}O_{23.46}$*
103 Oils	Polar	77.12	7.88	1.06	13.94	$C_{100}H_{121.74}N_{1.18}O_{13.57}$
103 Sol. Heavy Ends	Polar	80.76	6.61	1.86	10.77	$C_{100}H_{97.62}N_{1.98}O_{10.02}$
101 Oils	Total	85.31	8.31	0.58	5.80	$C_{100}H_{116.06}N_{0.58}O_{5.10}$
101 Sol. Heavy Ends	Total	85.87	5.88	1.65	6.60	$C_{100}H_{81.54}N_{1.65}O_{5.77}$
103 Oils	Total	82.23	7.98	0.78	8.01	$C_{100}H_{114.29}N_{0.81}O_{7.22}$
103 Sol. Heavy Ends	Total	85.98	6.05	1.75	6.22	$C_{100}H_{83.80}N_{1.75}O_{5.44}$

*Contaminated by phthalate plasticizer.

around mass 500 were observed. This result agrees with the maxima of mass 550 and 450 in the size exclusion chromatographic HPLC average molecular weight profiles from both Runs 101 and 103 (Table IV). There were a large number of both even and odd masses represented in profiles from both runs. Run 103 had a particularly prominent odd mass homologous series of 381, 395, 409, 423, 439, 453, and 467. The unit resolution of our quadrupole MS did not permit confirmation of these masses as aromatic nitrogen compounds, however they were tentatively assigned to neutral aromatic nitrogen compounds after considering the N/C ratios (Table V) and the separations used to obtain the fractions.

Soluble Heavy Ends-Polar Fractions. ^{13}C NMR and ^{1}H NMR spectroscopy (Figure 3, bottom) show a predominance of phenolic oxygen functionality in the soluble heavy ends polar fractions from both Runs 101 and 103. Although the total polar nitrogen content in the two runs was almost the same, the distribution of nitrogen compounds differed. The polar compounds from Runs 101 have a higher N/C ratio than those from Run 103 (Table V). Direct insertion probe MS heating profiles comparing the polar fractions from Runs 101 and 103 indicated a lower molecular weight range than that of the aromatic fractions, thus supporting the size exclusion chromatographic HPLC distribution (Table IV). Even and odd masses were plentiful within the molecular weight range found for heavy samples from Runs 101 and 103. A strong correlation between oxygen content (mostly phenolic) and viscosity for solvent-refined coals was noted in our laboratory but the same study failed to find a correlation between total nitrogen content and viscosity (6). At the present time it is not clear whether the differences found in nitrogen compound type distribution in the present study have any effect on viscosity.

Oils. Analysis of the oils from pass 40 of Runs 101 and 103 were carried out in order to provide comparison with the soluble heavy ends and to supply mass balance for the slurry separation analysis. A much more detailed characterization of the oils throughout the entire run is being prepared. The percentage of oils decreases from >85% in the solvents at the beginning of the runs to 45%-58% at the last pass. Differences in composition of the oils from Runs 101 and 103, pass 40, were assessed using the analytical procedures already described and solvent extraction (7). Base extraction of the phenols gave the same percent phenols for both Runs 101 and 103. The amounts of methylated phenanthrenes in the aromatic fraction of Run 103 were larger than in Run 101. The difference in the phenanthrene composition between Runs 101 and 103 pass 40 oils may be seen by observing the region between the resonances for unsubstituted phenanthrene hydrogens at 8.71 and 8.68 δ and the pyrene peak at 8.20δ in the 200 MHz ^{1}H NMR spectra at the bottom of Figure 4. The peaks between these values are characteristic of substituted phenanthrenes. The unsubstituted aromatic hydrocarbons, phenanthrene (8.71, 8.68 δ), fluorene (3.98δ), and acenaphthene (3.39δ) are more plentiful in Run 101 pass 40 oils than in Run 103 oils.

Pass to pass composition changes during the two recycle runs were observed (Table II, Figure 4). These changes are graphically displayed in Figure 4 which shows 200 MHz ^{1}H NMR spectra of some of the product oils as they change in composition from pass to pass. These changes are more evident during the initial dilution of startup solvent with product and become more subtle between the 30th and 40th

pass. The composition of product oil from both Runs 101 and 103 still appear to be changing slowly at pass 40.

Summary

A room temperature solubility separation method was used to separate the products of two 40 pass CPU runs that used different startup solvents. Although the composition was not investigated in detail, the insoluble heavy ends fraction from Run 101 appeared to contain binaphthyl while Run 103 did not. The oils and soluble heavy ends portions from the 40th pass were fractionated by silica gel column chromatography. The separation into alkanes, aromatics, and polars gave clean fractions based on NMR spectral data. The ^{1}H and ^{13}C NMR spectra of the corresponding oil and heavy fractions within a slurry sample resembled each other with oil polars (known to be mainly phenolic) resembling heavy polars and oil aromatics resembling heavy aromatics. The difference between oil and heavy polar fractions that causes them to be separated by solubility appears to be polarity rather than molecular weight differences. However, the major difference between oil and heavy aromatic fractions causing solubility separation is apparently due to molecular weight differences.

The success of these separations with materials of moderately high molecular weight makes possible a survey of a larger percentage of the liquefaction product slurry. The characterization of the fractions by a combination of techniques is now possible. A lack of high molecular weight model compounds to serve as knowns for further analysis presents a problem; however, additional work is in progress.

The products from Runs 101 and 103 after 40 passes were chemically dissimilar. Both the oils and the heavy ends showed a number of differences. It was of interest to note that the run started up with the PDU recycle solvent that contained more alkanes (13.9%) still yielded a product with more alkanes after 40 passes but the total amount was only 8% of the oil, 3.8% of the product slurry. The percent phenols in the oil (by extraction) was very close to equal for pass 40 from Runs 101 and 103 but the aromatic hydrocarbon character of the startup solvent appeared to be recognizable after 40 passes in both Runs 101 and 103. Run 103 still contains more alkylated and methylated aromatic hydrocarbons like the PDU solvent while Run 101 contained more unsubstituted aromatic hydrocarbons such as phenanthrene, acenaphthene, and fluorene like A04. There was an unequal distribution of nitrogen within the products from the two runs.

Various composition data were examined in an attempt to find a correlation with the much higher viscosity of Run 101. There did not seem to be much difference in the size of any heavy fraction when Runs 101 and 103 were compared, although the insoluble heavy ends were somewhat larger in Run 101 (29.8% of the slurry compared with Run 103 25.6%). The portion of the slurry that represents THF insoluble very heavy intractable organic matter was 7.5% for Run 101 and 6.7% for Run 103. The composition of the soluble heavy ends with respect to amounts of phenols and aromatics did not appear to be the cause of the viscosity. Only one difference was noted and that was Run 101 heavy ends polar fraction showed a higher N/C ratio indicating a different compound type distribution than Run 103. The viscosity difference could not be explained based on the oil composition. The percent phenols in the oil was the same in both Runs 101 and 103 although the polar (mainly phenolic) fraction of Run 101 also showed the higher N/C ratio indicating different compound types are present than in Run 103.

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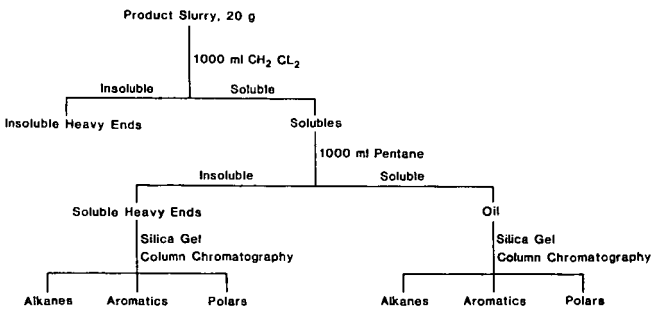

Figure 1. Separation of CPU product slurry by solubility and silica gel column chromatography.

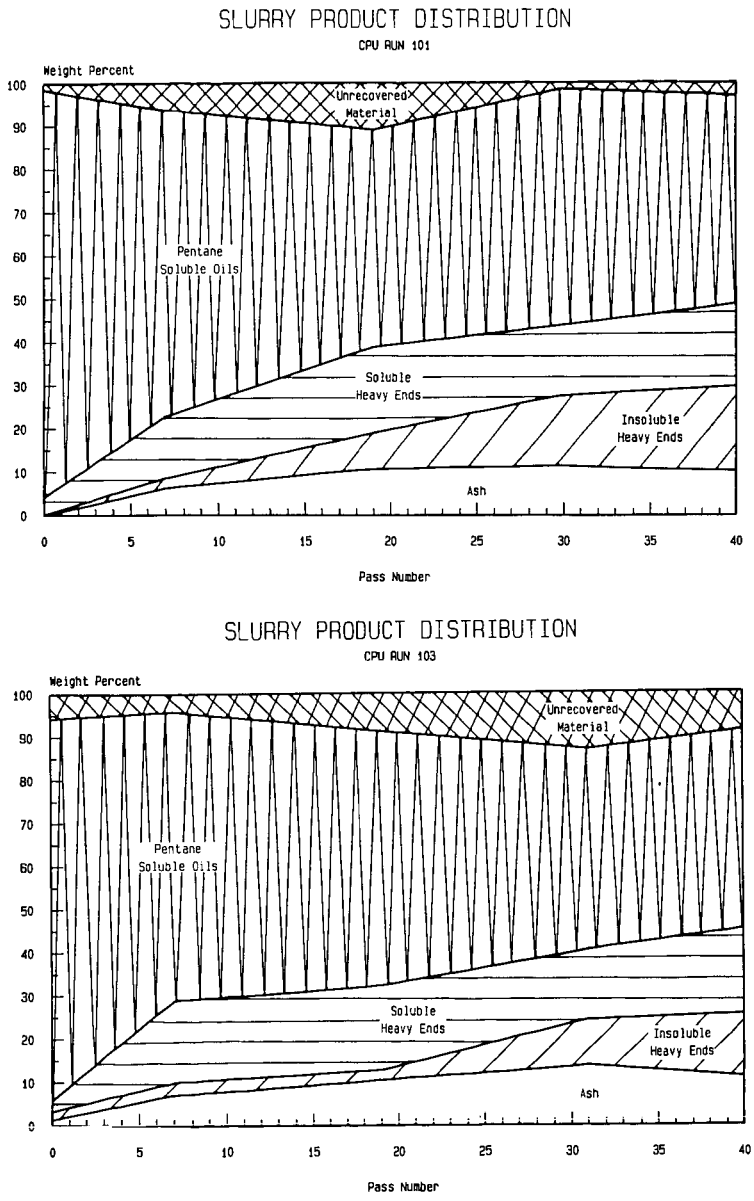

Figure 2. Product distribution as determined by solubility separation and ash analysis for CPU product slurries from Runs 101 and 103.

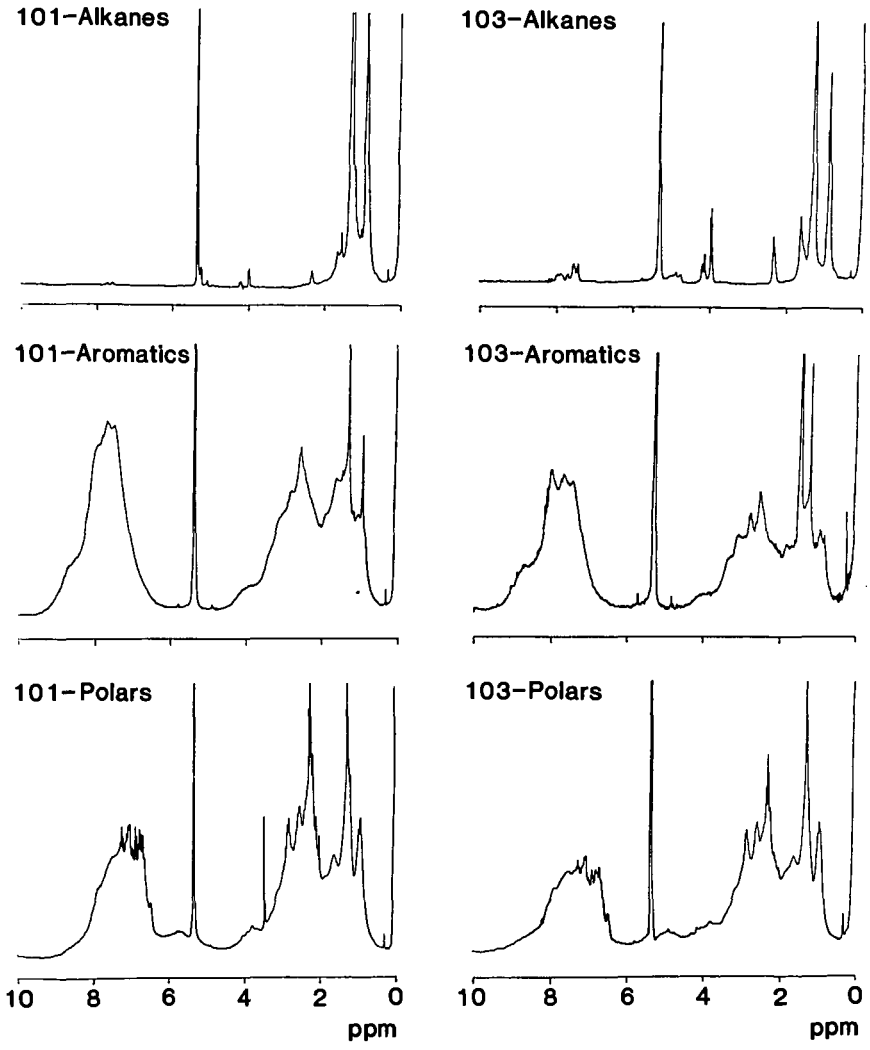

Figure 3. 200 MHz ^{1}H NMR spectra of silica gel column chromatographic fractions from soluble heavy ends, CPU Runs 101 and 103.

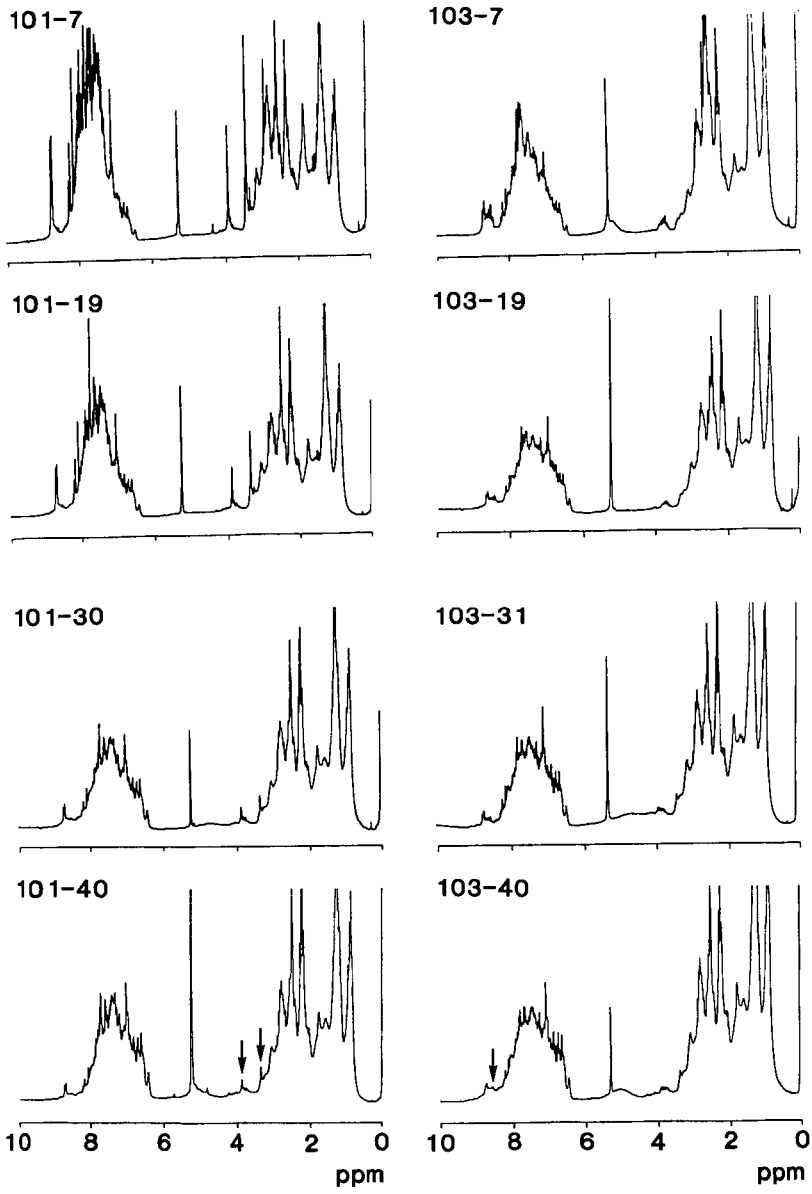

Figure 4. Changes in the oils during CPU Runs 101 and 103 as shown by 200 MHz ^{1}H NMR spectroscopy.